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A Stochastic Approach to Nucleation in Finite Systems

1. The considered model

The theory of first-order phase transitions, e.g. of condensation processes, include a variety of deterministic theories which describe sufficiently the dynamics of a given number of nuclei of the new phase (see e.g. /1-3/). But the initial formation of the nuclei is an intrinsic stochastic process and can't be explained in a deterministic sense.

Here we present a stochastic approach for a nucleation process in a finite system consisting of the formation of clusters by free particles /4,5/. Apart from other theories we fix the overall particle number N, the system volume V and the temperature T of the system:

$$N,\ V,\ T = \text{const.} \qquad (1)$$

Due to interactions between the particles the N particles will bound in clusters. Thus we have a particle configuration

$$\underline{N} = \{N_1\ N_2\ \dots\ N_l\ N_{l+1}\ \dots\ N_N\} \qquad (2)$$

where N_1 is the number of free particles and N_l $(l=2,\dots,N)$ the number of clusters with l bound particles. $\underline{N}$ describes the cluster distribution in the finite system. Because of (1) it helds

$$N = \sum_{l=1}^{N} l\ N_l \ ;\ 0 \leqslant N_l \leqslant \frac{N}{l}\ (l=1,\dots,N) \qquad (3)$$

In the following we are interested in the probability $P(\underline{N},t)$ to find a given cluster distribution $\underline{N}$ at the time t.

The time evolution of $P(\underline{N},t)$ can be described by a Master equation /4,5/:

$$\frac{\partial}{\partial t} P(\underline{N},t) = \sum_{\underline{N}'} w(\underline{N}|\underline{N}')P(\underline{N}',t) - w(\underline{N}'|\underline{N})P(\underline{N},t) \qquad (4)$$

$\underline{N}'$ specifies those distributions which are attainable from the assumed distribution $\underline{N}$ with the transition probabilities per unit time $w(\underline{N}'|\underline{N})$.

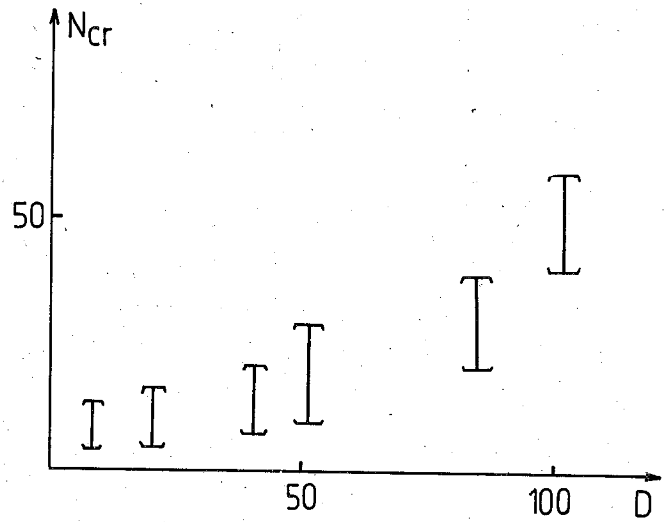

Fig. 5: Critical particle number N_{cr} for various D

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2. The equilibrium probability distribution

The equilibrium state is characterized by the condition of detailed balance:

$$w(\underline{N}'|\underline{N})P^{o}(\underline{N}) = w(\underline{N}|\underline{N}')P^{o}(\underline{N}') \tag{5}$$

where $P^{o}(\underline{N})$ is the equilibrium probability of the distribution $\underline{N}$. The maxima of $P^{o}(\underline{N})$ denote the equilibrium cluster distribution in agreement with the deterministic theory.

$P^{o}(\underline{N})$ is given by the following relation /4/:

$$P^{o}(\underline{N}) = \frac{1}{Z(T,V,N)} \exp\left\{-\frac{1}{k_B T} F(T,V,\underline{N})\right\} \tag{6}$$

Here $Z(T,V,N)$ is the canonic partition function of the interacting N particle system. It is a constant and stands for the normalization. $F(T,V,\underline{N})$ is the free energy of the considered cluster distribution $\underline{N}$ assuming the clusters and free particles as an ideal mixture /4,5/:

$$F(T,V,\underline{N}) = \sum_{l=1}^{N} N_l \left\{ f_l + k_B T \left(\ln \frac{N_l}{V} \lambda_l^3 \quad -1\right)\right\} \tag{7}$$

$F(T,V,\underline{N})$ considers the partial pressure of the clusters and free particles and the mixing entropy (see also /6/). λ_l is the de-Broglie wave length. f_l is a potential term which includes the binding energy of the cluster and the surface energy. For large clusters we choose /4/:

$$f_l = -Al + Bl^{2/3} \tag{8}$$

while for small clusters

$$f_l = -\frac{A}{2}\, l\, (l-1) \tag{9}$$

is hold /5/. A and B are temperature depending constants /7/:

$$A = -k_B T \ln \frac{p_\infty}{k_B T} \lambda_1^3 \;; \quad B = 4\pi \left(\frac{4\pi}{3} c_\alpha\right)^{-2/3} \sigma \tag{10}$$

with σ being the surface tension of the cluster, c_α the particle density in the cluster, p_∞ the saturation pressure over a macroscopic flat liquid surface.

References

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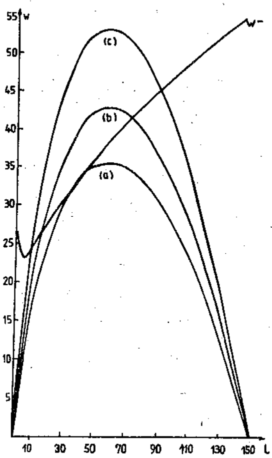

Fig. 1: Transition probabilities w_1^+ and w_1^- (15) vs. cluster size l

(a) y_o = 3.86 (b) y_o = 4.63 (c) y_o = 5.79

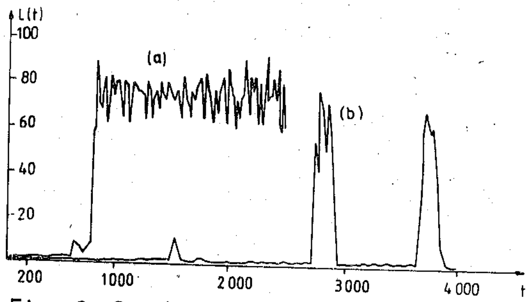

Fig. 2: Stochastic evolution of the cluster size l vs. time t (in time units)
(a) $y_o = 4.36$ (b) $y_o = 4.21$

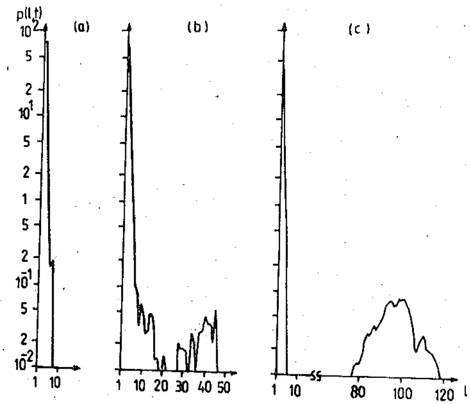

Fig. 3: Distribution of clusters of size l during a given time t (in time units)
R - number of elementary reactions (11), $y_o = 7.5$
(a) $R = 5\cdot10^2$; $t = 0.452$
(b) $R = 5\cdot10^3$; $t = 4.946$
(c) $R = 5\cdot10^4$; $t = 143.551$

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Isoenergetic Nucleation in Finite Systems

In this paper we consider the kinetics of nucleation under different thermodynamic boundary conditions. This contribution is based on investigations concerning the condensation of liquid drops from a supersaturated vapour under isothermic-isochoric boundary conditions /1/. We use here the same droplet model as for the isothermic case, which is described in detail elsewhere /1-3/. The dynamics of isothermic nucleation (condensation of water droplets with fixed temperature and volume of the system) is summarized in Fig. 1.

In the following we consider an ensemble of clusters with the distribution $\underline{N} = (N_1, N_2, \ldots, N_n, \ldots, N_n)$ in a finite system $M_o = \sum_1 n\, N_n$ = const. The theory starts with the following free energy as state function comming from statistics ($F=-kT \ln Z$, ideal gas)

$$F(T,V,\underline{N}) = -\frac{3}{2}\, kTN_o \ln T/T_o - kTN_o \ln V/V_o + kT\sum_1 N_n \ln N_n - kTN_o - \frac{3}{2}\, kT\sum_1 N_n \ln n + \sum_2 N_n f_n(T) \quad (1)$$

with the reference values T_o = 293 K, $V_o = (h/\sqrt{2\pi mkT_o})^3 \approx 1.4 \cdot 10^{-5}\,nm^3$ and $N_o = \sum_1 N_n$ as overall number of particles. The function $f_n(T)$ gives the potential contributions of a size-n-cluster. Taking into account bulk ($\mu_\infty(T) \cdot n$) and surface ($\sigma A(n)$) terms we use (compare /2,3/)

$$f_n(T) = \mu_\infty(T) \cdot n + \sigma A(n) \quad (2)$$

with $\mu_\infty(T) = -\frac{3}{2}\, kT \ln T/T_o + kT \ln(c_{eq}(T) V_o)$ (2a)

and $c_{eq}(T) = c_o (T/T_o)^{-1} \exp\{\varepsilon\,(1/T_o - 1/T)\}$ (ε =5000 K) (2b)

Inserting (2) in (1) we get

$$F(T,V,\underline{N}) = -kT(\frac{3}{2}N_o + \frac{5}{2}M_\alpha) \ln T/T_o - kTN_o \ln V/V_o + kT\sum_1 N_n \ln N_n - kTN_o - \frac{3}{2}kT\sum_1 N_n \ln n + \sigma A_\alpha + kTM_o \ln c_o V_o + k\,\varepsilon\, M_\alpha T/T_o - k\,\varepsilon\, M_\alpha \quad (3)$$